Screening de contaminantes emergentes, metabolitos y productos de degradación en aguas mediante técnicas avanzadas de análisis

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Analytical Challenges in Environmental Research

Thousands of environmental (organic) contaminants of very different physico-chemical characteristics

Metabolites and Transformation/Degradation Products

Investigation of **new (unknown) contaminants** potentially dangerous for the environment

Reliable **detection, identification** and accurate **quantification** in samples

- **Well-established analytical (quantitative) methods for many priority contaminants**

  - Quantitative analysis based on **tandem MS** (GC & LC)

  - Good sensitivity and selectivity: low LODs and LOQs

- Need to **advance in HRMS strategies** for investigation of large number of compounds

  - Wide-scope screening methodologies (target, suspect, non-target)

Aquatic environment is a highly complex scenario

  - Thousands of potential contaminants
  - Low concentrations
  - Many TPs still unknown
  - General lack of data

Ideal wide-scope universal screening does not exist

⬇

Impossible to detect all potential contaminants in the samples

⬇

Limitations associated to sample treatment and meaurement (e.g. chromatographic conditions)

Sample treatment

Measurement

Some compounds require specific conditions (e.g. highly volatile, highly polar/ionic)

Screening of organic contaminants

The closest approach to the "universal" screening

⬇

Combined use of GC and LC both coupled to HRMS

TOF

Orbitrap

Q-TOF

GC - HRMS

LC - HRMS

Non polar-medium polar
Volatile compounds
Thermally stable

Polar-ionic compounds
Non-volatile
Thermally unstable

LTQ
Orbitrap

Magnetic
sector

Q-Orbitrap

GC
(APCI)

QTOF

(UHP)LC
(ESI, APCI)

Screening of environmental samples

Why High Resolution Mass Spectrometry?

Full spectrum acquisition	High Resolution	Accurate mass data
⬇	⬇	⬇
Molecular ion/protonated molec Fragments/product ions	Less mass interferents coeluting matrix components	High mass accuracy (low mass errors)
⬇	⬇	⬇
Powerful tool for identification and confirmation	Resolve interefences Lower LODs	Elemental composition and chemical structure

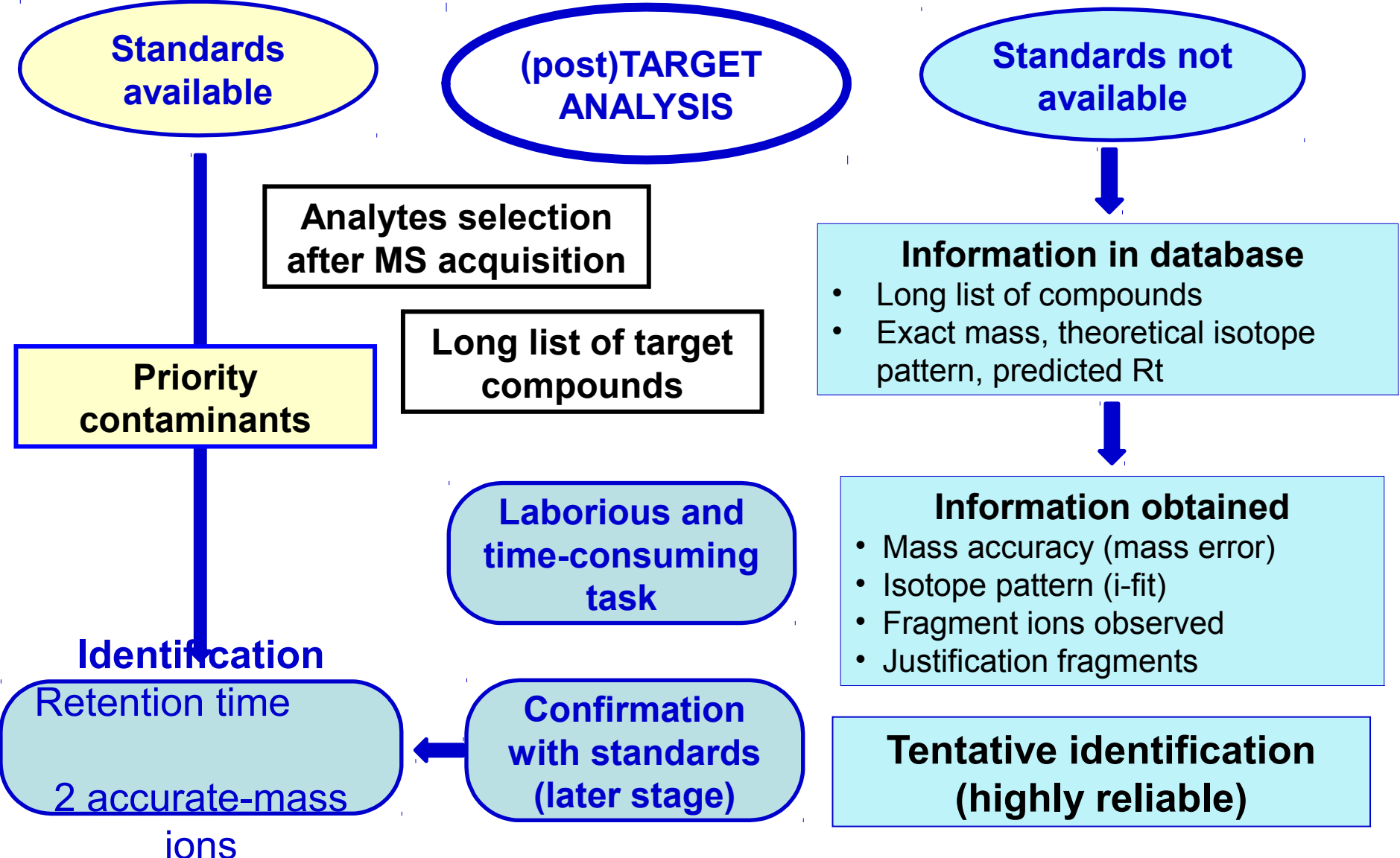**TARGET SCREENING**   **SUSPECT SCREENING**   **NON-TARGET SCREENING**
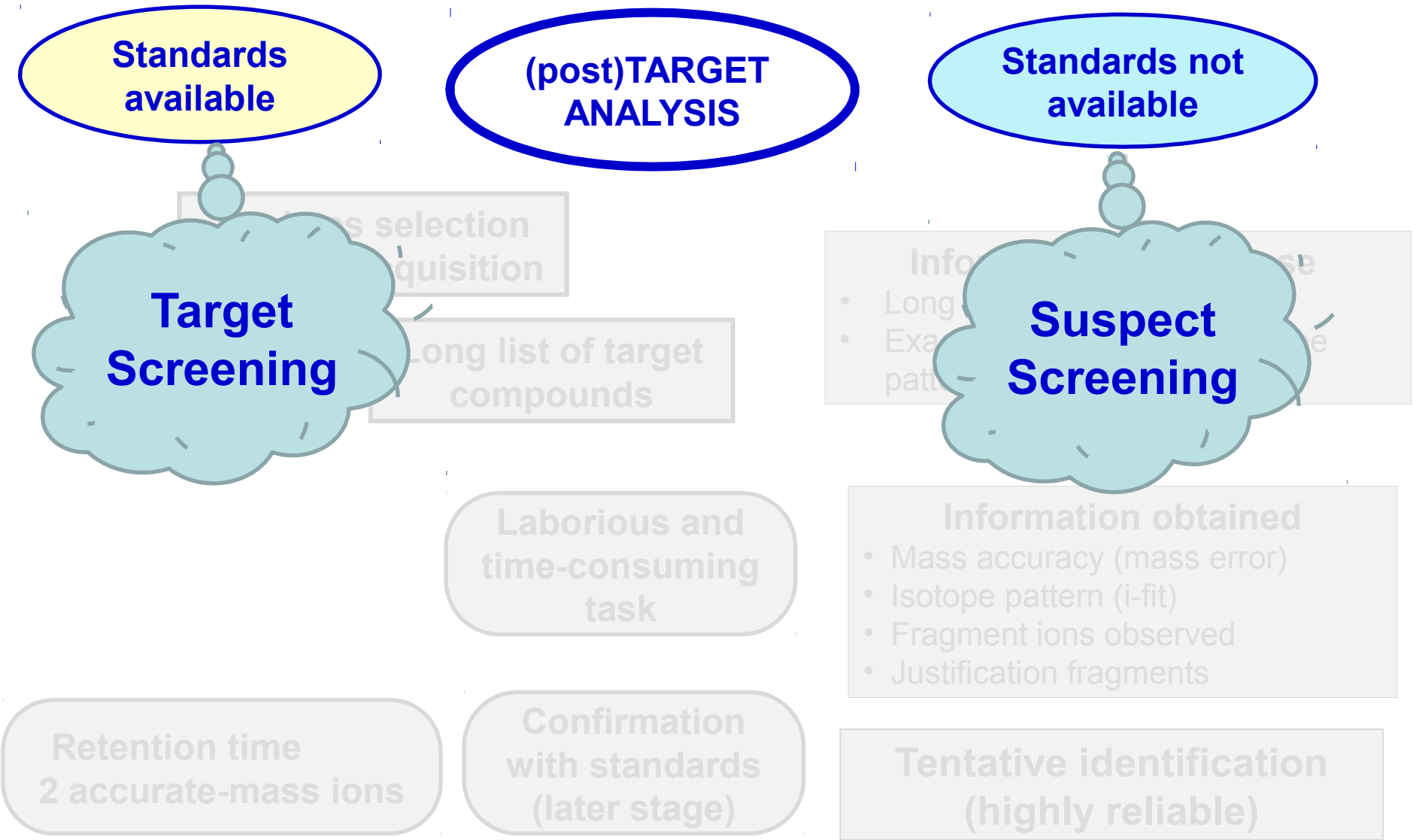
RETROSPECTIVE ANALYSIS

QTOF MS
Efficiently used for wide-scope screening

Standards available

(post)TARGET ANALYSIS

Standards not available

Analytes selection after MS acquisition

Priority contaminants

Long list of target compounds

Information in database
- Long list of compounds
- Exact mass, theoretical isotope pattern, predicted Rt

Laborious and time-consuming task

Information obtained
- Mass accuracy (mass error)
- Isotope pattern (i-fit)
- Fragment ions observed
- Justification fragments

Identification

Retention time

2 accurate-mass ions

Confirmation with standards (later stage)

Tentative identification (highly reliable)

QTOF MS
Efficiently used for wide-scope screening

Standards available

(post)TARGET ANALYSIS

Standards not available

Target Screening

Suspect Screening

Mass selection acquisition

Long list of target compounds

Info

Long
Exa
patt

Laborious and time-consuming task

Information obtained
- Mass accuracy (mass error)
- Isotope pattern (i-fit)
- Fragment ions observed
- Justification fragments

Retention time
2 accurate-mass ions

Confirmation with standards (later stage)

Tentative identification (highly reliable)

(post)target screening using QTOF MS

Water Samples

Generic, simple sample treatment

Obviously, sample procedure can be modified/ improved
- minimize losses of VOCs
- pH adjustments
- additional treatments to recover highly polar compounds

octyl/nonyl phenols, pesticides…

UV filters, hormones, metabolites/TPs

Searching for around 3,000 compounds

- **Detection**
- **Identification (standards)/tentative identification**

Qualitative validation for ~ 320 model compounds

UHPLC-QTOF screening in wastewater

EDDP
Metabolite methadone
$C_{20}H_{24}N$

MH+ = 278.1906

Confirmed with standard
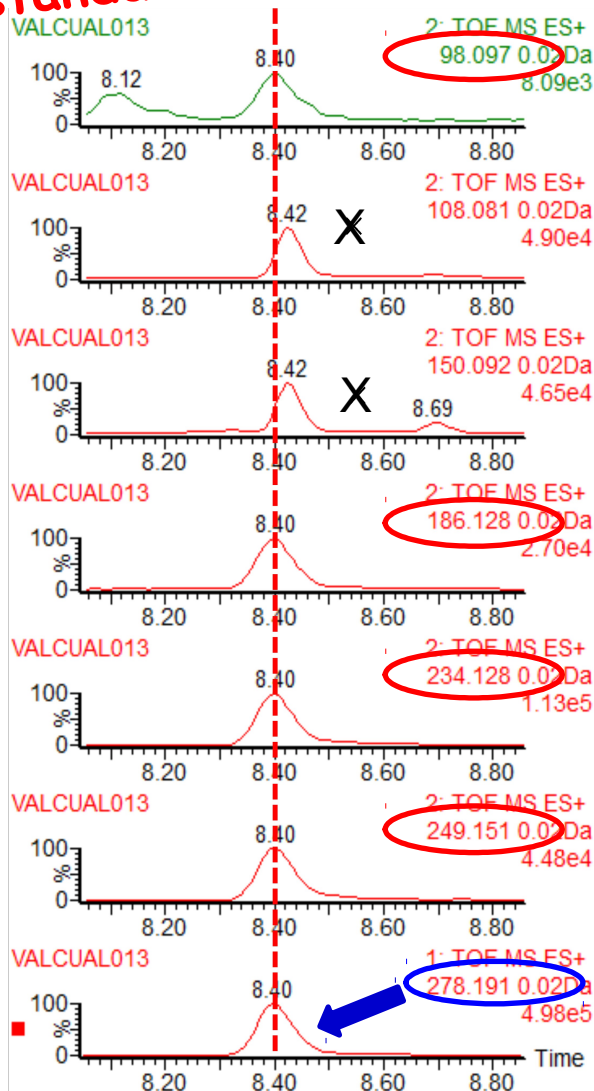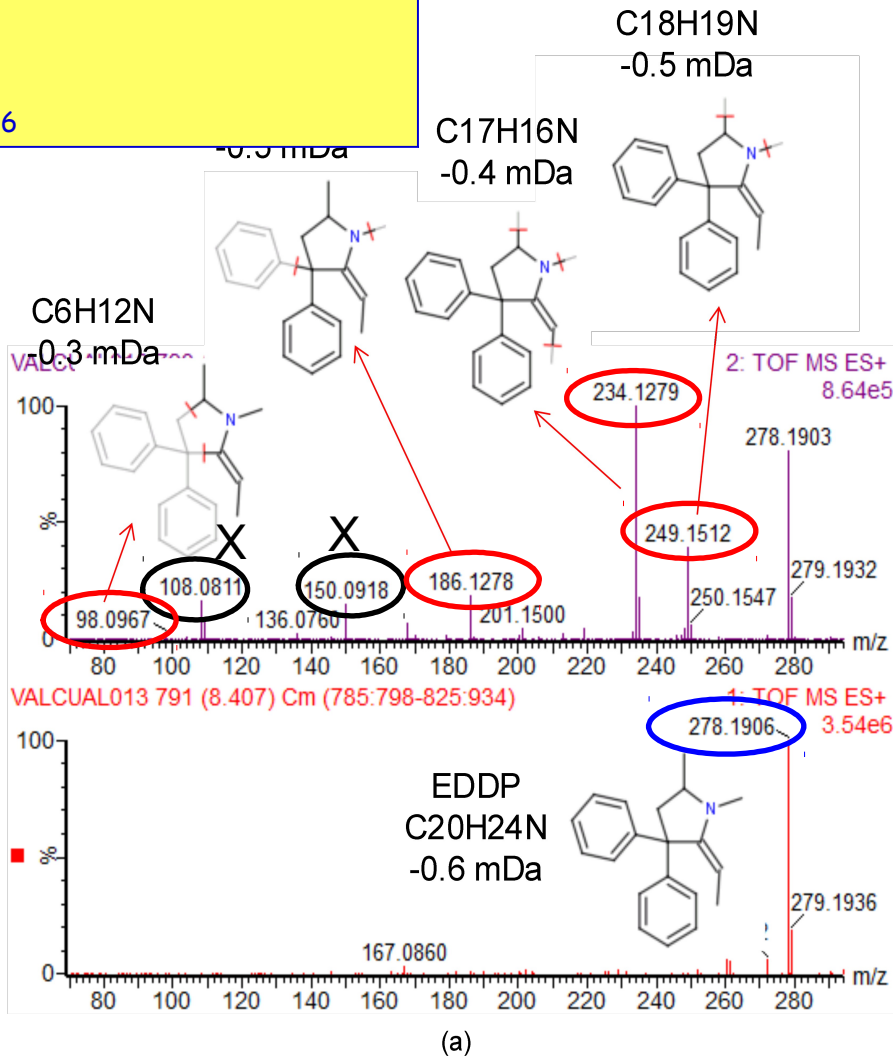
(✕) indicates that this ion is not related with EDDP.

78 pesticides (metabolites/TPs); 24 pharmaceuticals (metabolites/TPs)
4 drugs abuse; 4 preservatives; 5 UV-filters; 2 sweeteners
3 PAHs; 3 musks; 2 X-ray agents;1 antimicrobial; 2 insect repellents

The most frequently detected

Pesticides
Triazine herbicides (particularly, terbuthylazine and terbutryn)
Insecticides diazinon and chlorpyrifos-ethyl
Fungicides thiabendazol, carbendazim and propiconazole

Pharmaceuticals
Antibiotic ofloxacin
Anti-inflammatory/analgesic diclofenac
Angiotensin II receptor antagonists valsartan and irbesartan
Antidepressant venlafaxine
Anti-epileptic carbamazepine

Others
Benzoylecgonine (the main metabolite of cocaine)
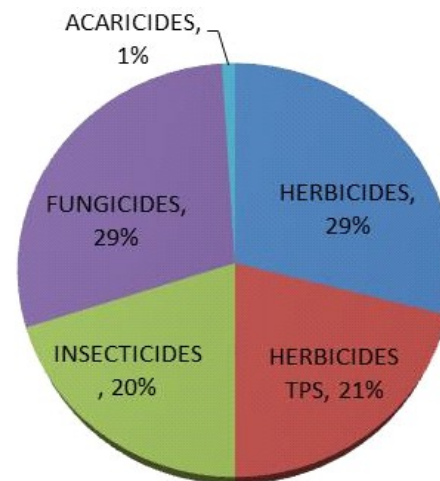Tonalide (musk) and octocrylene (UV filter)

Positive findings in ground water and surface water by combined screening using GC(APCI)-QTOF MS and UHPLC(ESI)-QTOF MS.
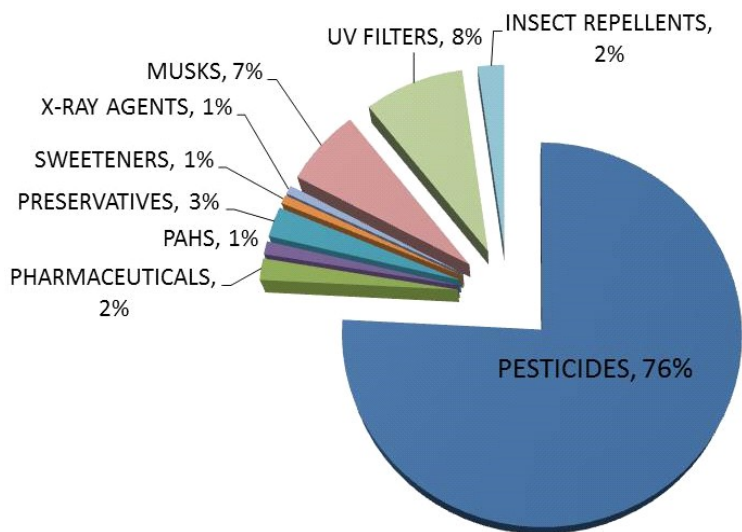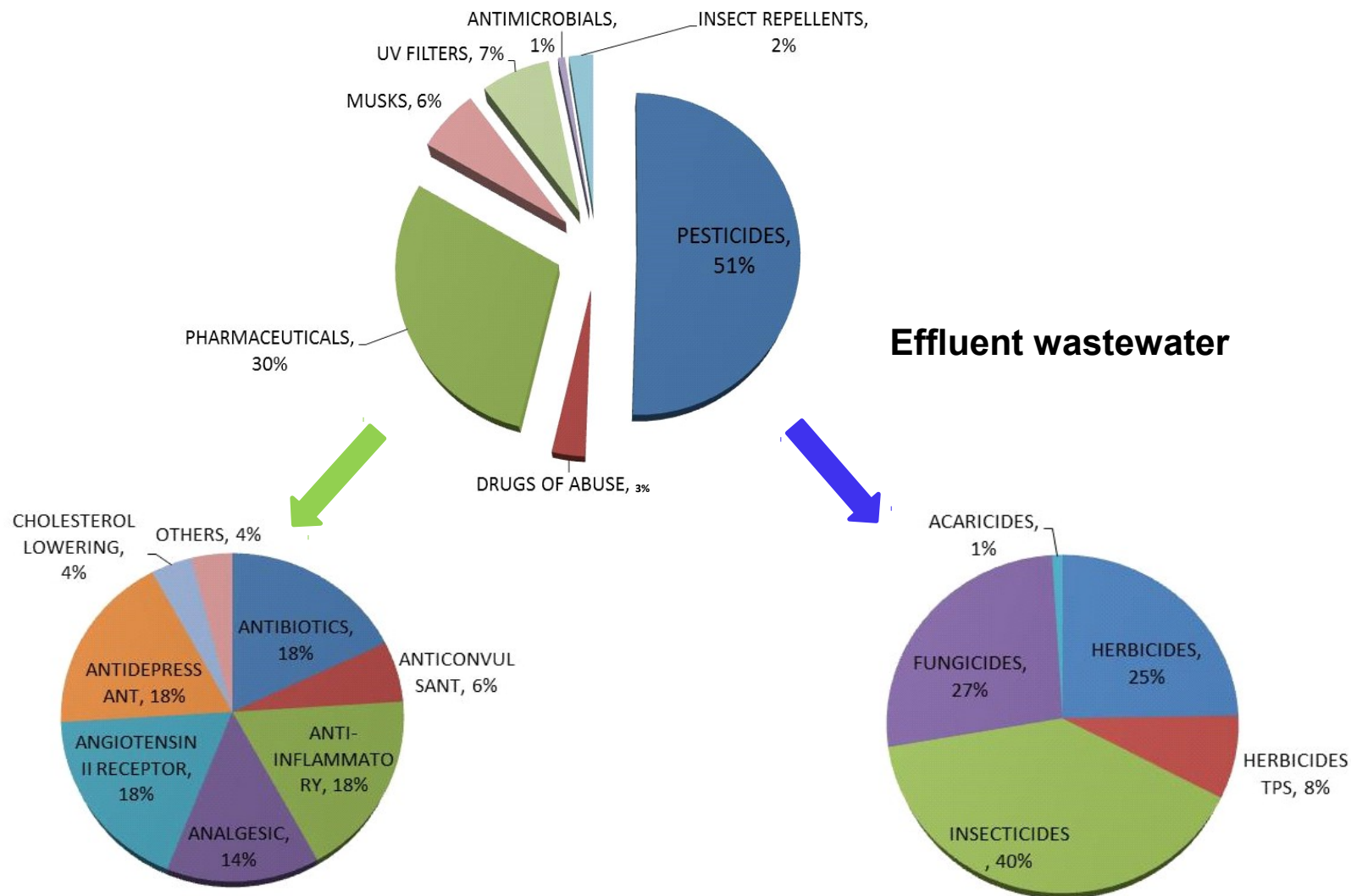

GROUNDWATER
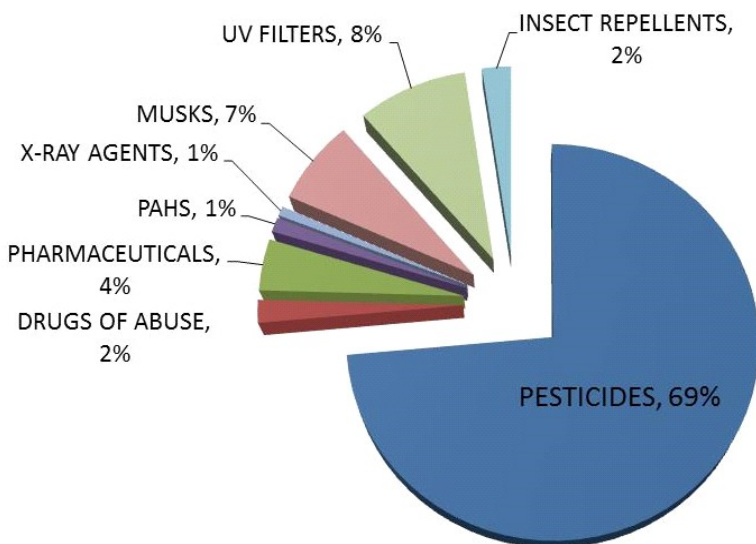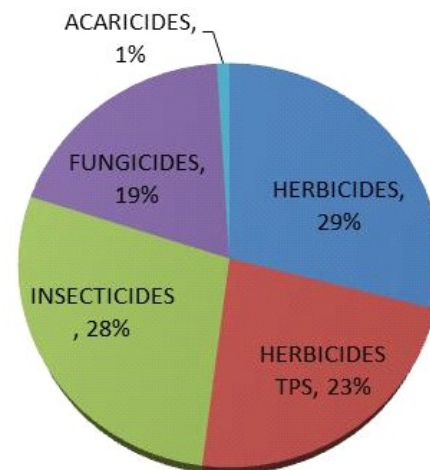
SURFACE WATER

Positive findings in effluent wastewater by combined screening using GC(APCI)-QTOF MS and UHPLC(ESI)-QTOF MS.

Effluent wastewater

Relevance of metabolites/TPs research

➢ Many still unknown

➢ Few data available on their presence in the environment

➢ Most of them unregulated

➢ Lack of reference standards

➢ General lack of toxicological data

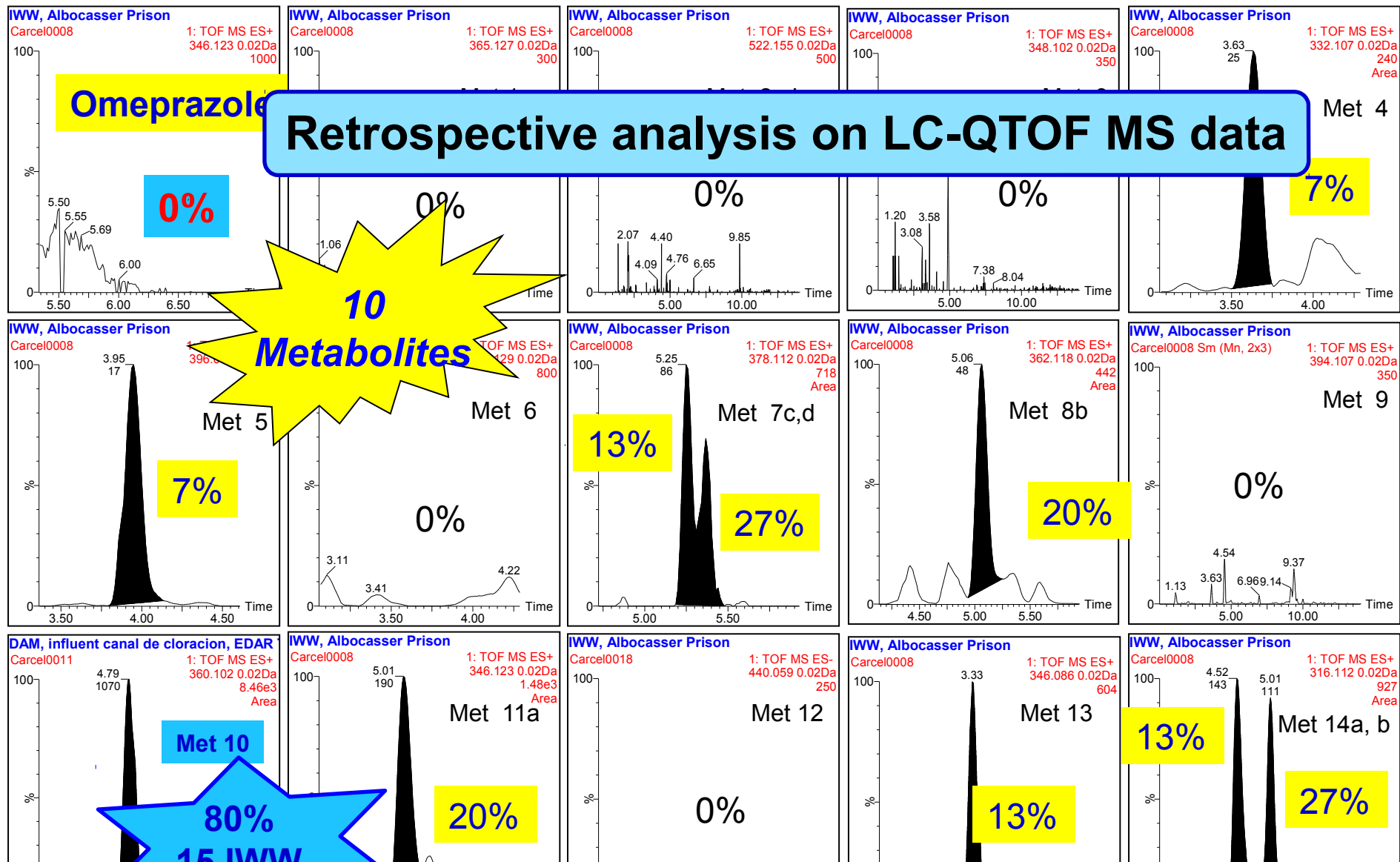➢ Concentration data required for appropriate risk assesment

Analytical challenge, commonly directed towards the identification/discovery of the compound

Once the compound is detected and identified quantitative data would be required in additional analysis (e.g. LC-MS/MS QqQ)

Searching for **non-targeted** metabolites/TPs

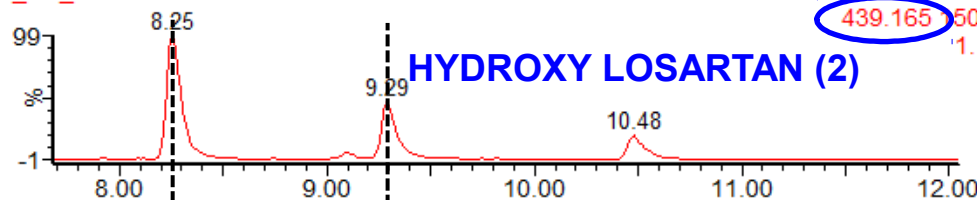## ➤ Laboratory degradation/metabolism experiments

Retrospective analysis on LC-QTOF MS data

10 Metabolites

Omeprazole — 0%

Met 1 — 0%

Met 2 — 0%

Met 3 — 0%

Met 4 — 7%

Met 5 — 7%

Met 6 — 0%

Met 7c,d — 13% / 27%

Met 8b — 20%

Met 9 — 0%

Met 10 — 80% 15 IWW

Met 11a — 20%

Met 12 — 0%

Met 13 — 13%

Met 14a, b — 13% / 27%

ePTAR06
RB_NR_0070

HYDROXY LOSARTAN (1)

1: TOF MS ES+
439.165 50PPM
1.16e5

C22H24N6O2Cl   +16

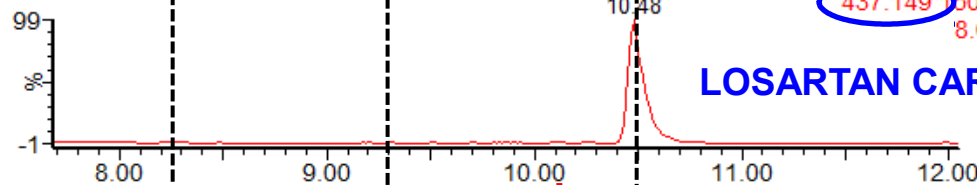LE   (d)

HYDROXY LOSARTAN (2)

8.25
9.29
10.48

RB_NR_0070

1: TOF MS ES+
437.149 50PPM
8.01e4

C22H22N6O2Cl   +14

LE   (c)

LOSARTAN CARBOXYLIC ACID

10.48

RB_NR_0070

2: TOF MS ES+
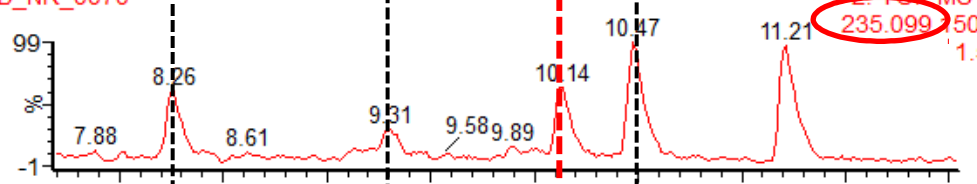190.065 50PPM
1.00e4

Fragment 3

ESI +

7.70
8.26
9.28
10.12
10.47
11.20
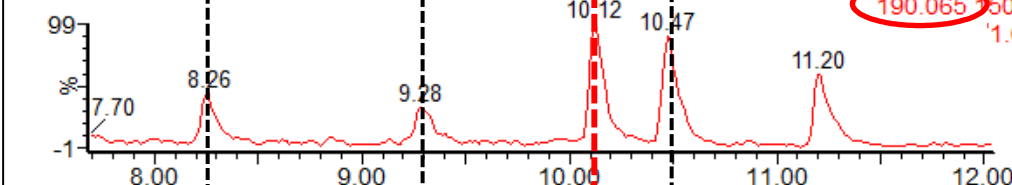
RB_NR_0070

2: TOF MS ES+
235.099 50PPM
1.54e4

HE   (b)

Fragment 2

7.88
8.26
8.61
9.31
9.58 9.89
10.14
10.47
11.21

RB_NR_0070

2: TOF MS ES+
207.092 50PPM
1.59e5

Fragment 1

8.25
9.29
10.12
10.47
10.87
11.21
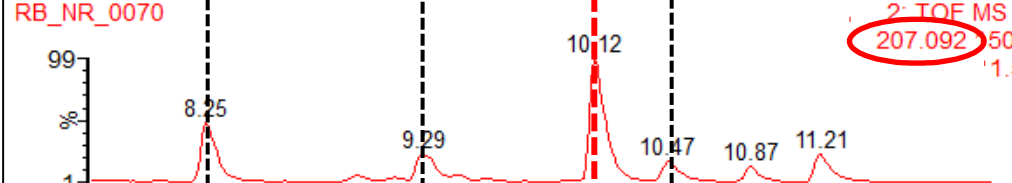
RB_NR_0070

1: TOF MS ES+
423.169 50PPM
2.63e5

C22H24N6OCl

LE   (a)

LOSARTAN

10.13

[M+H]⁺

Time

CONCLUSIONS

- **Combined use of GC and LC** coupled to **QTOF MS:** powerful approach for **large-scope screening** of organic contaminants in the environment, emerging contaminants included

- **Accurate-mass full-spectrum data** provided by TOFMS allow easily increase the number of compounds searched: **retrospective analysis**

- **Metabolites and TPs are commonly present in the aquatic environment**, even more than the parent compounds. They can be discovered using different approaches, as searching for common fragments, in-silico prediction tools or laboratory experiments

- Despite advances, still many **"difficult" compounds** (e.g. highly volatile and highly polar/ionic) **require specific methods** with different sample treatment and measurement conditions

- **Large databases** of compounds of interest, including metabolites/TPs, and **(accurate) mass spectral libraries are** required
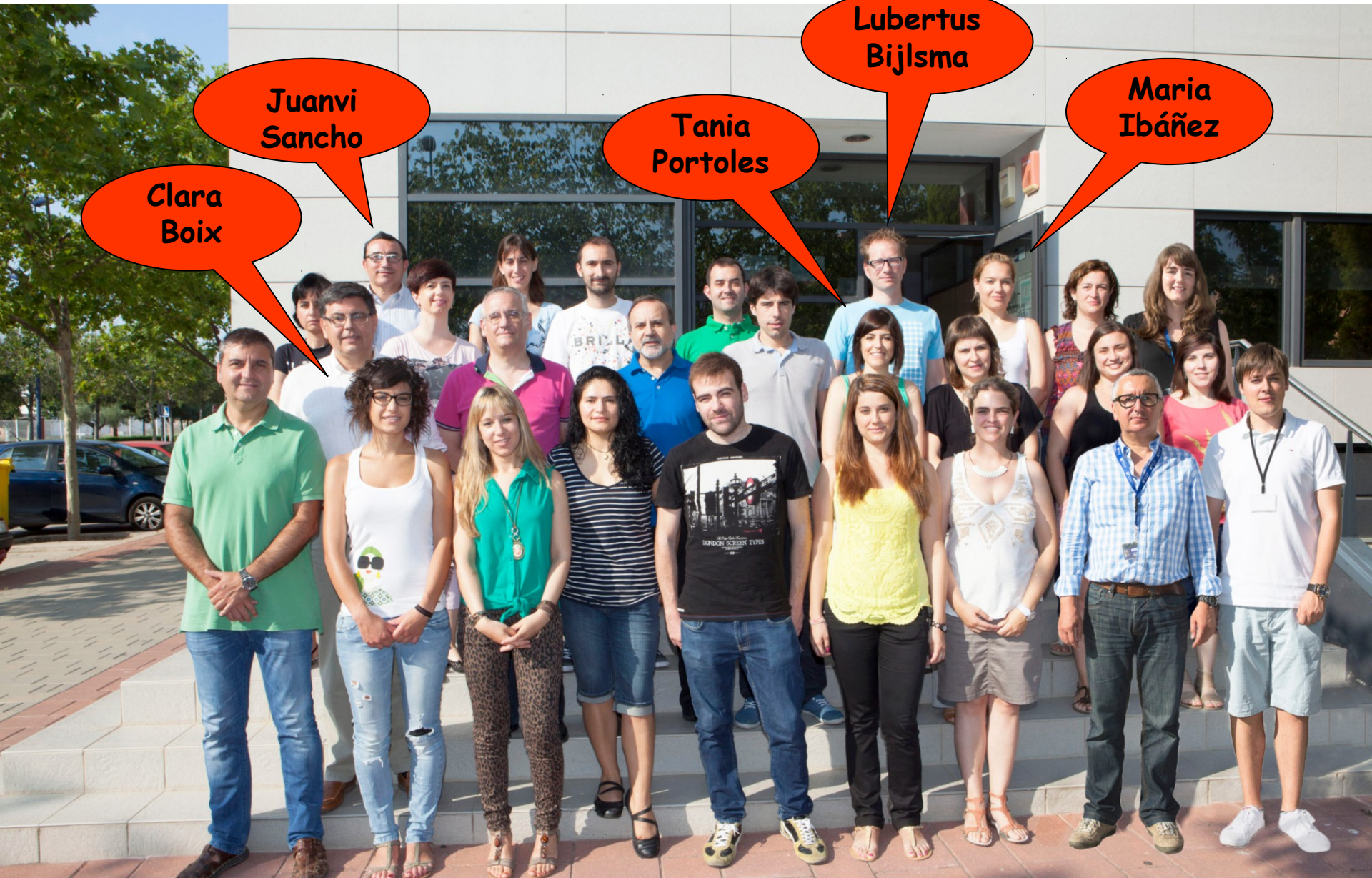
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Thank you for your attention!

Questions

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